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(54) Title: TIRE SIDEWALL COMPOSITION

(57) Abstract

A tire sidewall composition having improved properties is provided. The composition comprises a halogen-containing copolymer of a C<sub>4</sub> to C<sub>7</sub> isomonoolefin and a para-alkylstyrene, and an unsaturated rubber, such as natural rubber. Tires comprising the sidewalls are also provided.

TIRE SIDEWALL COMPOSITIONBACKGROUND OF THE INVENTION1. Field of the Invention

The present invention relates to tire sidewall compositions which exhibit improved ozone resistance and fatigue crack propagation resistance, as well as good sidewall adhesion to the tire carcass and good heat build-up.

2. Description of Information Disclosures

Rubber tires, such as pneumatic tires, include many components, such as, for example, sidewalls, which may be decorative and may have incorporated therein a titanium dioxide pigment. Sidewalls are continuously subjected to distortion under the normal road operating conditions, and the sidewalls are subjected to extensive continuous flexing and can crack under such flexing conditions. In addition to such flex cracking, such sidewalls are also subjected to atmospheric chemical action such as by ozone attack. The overall effect is that the sidewalls may erode and degrade and can even separate from the tire carcass during use and can cause the tire to fail.

Generally, the current practice in the manufacture of black sidewalls is to add chemical protectants to general purpose rubbers in an attempt to minimize ozone and flex cracking but they tend to be fugitive and staining in the case of contact with white sidewalls combination. In some

U.S. Patent No. 3,830,274 to Waser, Jr., assigned to The Goodyear Tire and Rubber Company, discloses yet another elastomer blend for use in pneumatic tire sidewall compositions, which contains an ethylene propylene non-conjugated diene terpolymer along with bromobutyl rubber and a cis-1,4 polyisoprene rubber such as natural or synthetic rubber, along with a rubbery cis-1,4 polybutadiene with a specified molecular weight distribution. The patentee states that this blend provides substantially improved hot flex-life and carcass adhesion properties for tire sidewalls.

U.S. Patent 4,224,196 discloses a sidewall composition having improved flex resistance, wherein the blend composition comprises a blend of a halobutyl rubber, a highly unsaturated rubber and an oil extended EPDM terpolymer.

There is still a need for improvement in properties of tire sidewalls.

#### SUMMARY OF THE INVENTION

The present invention relates to tire sidewall compositions which comprise a blend composition of at least one highly unsaturated rubber, and a brominated copolymer of an isoolefin and a para-alkylstyrene, wherein the blend compositions exhibit improved ozone resistance and fatigue crack propagation resistance as well as good sidewall adhesion to the tire carcass, good heat build-up, and good aging characteristics, wherein the compositions may additionally optionally include an EPDM terpolymer and/or halobutyl rubber.

In a preferred embodiment of the present invention the sidewall composition comprises from about 10 to about 90 parts of a highly unsaturated rubber such as of natural rubber, and from about 10 to about 90 parts of brominated copolymer of an isoolefin and a para-alkylstyrene, wherein

employing the halogenated copolymer of isoolefin and para-alkylstyrene in blends with general purpose rubber (GPR), i.e., highly unsaturated, one obtains improved ozone resistance and fatigue crack propagation of these compositions as well as improved sidewall adhesion.

It has also been found that compositions having desirable characteristics can be obtained by utilizing the halogenated para-alkylstyrene copolymer with only one other unsaturated rubber such as natural rubber in the absence of other rubber components. This is particularly effective in white sidewall formulations.

The tire sidewall composition of the present invention comprises blend compositions of from about 10 to about 90 parts by weight per hundred of total rubber content of at least one highly unsaturated rubber selected from the group consisting of natural rubber, SBR rubber, polyisoprene and polybutadiene rubber, preferably about 20 to about 80, more preferably about 30 to about 70; and from about 10 to about 90 parts per hundred of a halogenated copolymer of an isoolefin and a para-alkylstyrene, wherein the halogen is bonded to the para-alkyl group of the para-alkyl styrene unit, more preferably about 15 to about 85 and most preferably about 20 to about 80 parts; for example, about 30 to about 70 parts. In particularly preferred compositions useful in tire sidewalls, the halogenated copolymer comprises at least about 35 to about 75 parts, for example, 40 parts, and the highly unsaturated rubber comprises natural rubber and/or polybutadiene rubber. The blend composition may also optionally include from about 1 to about 90, preferably about 5 to about 40 parts of halobutyl rubber and/or from about 1 to about 40 parts, preferably about 5 to about 20 parts per hundred of EPDM. When white sidewalls are desired, particularly preferred compositions comprise the halogenated para-alkylstyrene copolymers and natural rubber in a weight ratio of halogenated para-

saturated backbone of methylene linkages with the non-conjugated diolefin, e.g. dicyclopentadiene or substituted norbornene, attached so as to provide unsaturated side chains with readily available crosslinking sites for sulphur curing. The EPDM elastomers thus contain a fully saturated backbone which provides outstanding resistance to oxidation, ozone, and cracking, as well as excellent low temperature flexibility. The Mooney viscosity of the EPDM terpolymer as measured at 125°C is about 20 to 80, more preferably about 25 to 75 and most preferably about 40 to about 60. The ethylene content of the EPDM terpolymers may range from about 20 to about 90 weight percent, preferably from about 30 to about 85, more preferably from about 35 to about 80 weight percent. The total diene monomer content in the EPDM terpolymers may suitably range from about 0.1 to about 15 weight percent, preferably from about 0.5 to about 12 weight percent.

The non-conjugated dienes may be straight chain or cyclic hydrocarbon diolefins having from 6 to 15 carbon atoms, such as dicyclopentadiene, tetrahydroindene, including alkyl substituted tetrahydroindenes, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, 2-methyl-norbornadiene, 2,4-dimethyl-2,7-octadiene, 1-4-hexadiene, 5-ethylidene-2-norbornene, and 3-methyl cyclopentene. The most preferred compounds include 5-methylene-2-norbornene, dicyclopentadiene, 1,4-hexadiene, 5-ethylidene-2-norbornene, and 4,7,8,9-tetrahydroindene. A preferred EPDM terpolymer of the present invention is Vistalon® 6505 manufactured by Exxon Chemical Company.

The term "butyl rubber" as employed herein is intended to refer to a vulcanizable rubbery copolymer containing, by weight, from about 85 to 99.5% combined isoolefin having from 4 to 8 carbon atoms and .5 to 15% combined conjugated diolefin having 4 to 8 carbon atoms. Such copolymers and their preparation are well known. The isoolefin, such as

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The butyl rubber may be halogenated by means known in the art. The solid rubber may be reacted in an extruder using halogen gas or on a hot rubber mill or internal mixer with a compound which releases halogen such as N-halo-succinimide and N-halo-hydantoin. Alternatively, the butyl rubber may be dissolved in an inert hydrocarbon solvent such as pentane, hexane or cyclohexane and halogenated by addition to the solution of elemental chlorine or bromine. In a typical commercial process, butyl rubber is dissolved in a solvent to form a solution containing from about 5 to about 30 weight percent of rubber. Elemental chlorine or bromine is added to the solution, at a temperature of 0° to about 100°C, in sufficient quantity that the chlorinated or brominated rubber recovered contains up to 1 atom of chlorine or up to 3 atoms of bromine per carbon-carbon double bond originally in the butyl rubber.

The Mooney viscosity of the halobutyl rubbers useful in the instant invention as measured at 125°C (ML 1+4) range from about 20 to about 80, more preferably about 25 to about 55, and most preferably about 30 to about 50.

Suitable halogen-containing copolymers of a C<sub>4</sub> to C<sub>7</sub> isomonoolefin and a para-alkylstyrene for use as a component of the present tire sidewall composition comprise at least 0.5 weight percent of the para-alkylstyrene moiety. For elastomeric copolymer products, the para-alkylstyrene moiety may range from about 0.5 weight percent to about 20 weight percent, preferably from about 1 to about 20 weight percent, more preferably from about 2 to about 20 weight percent of the copolymer. The halogen content of the copolymers may range from above zero to about 7.5 weight percent, preferably from about 1.0 to about 7.5 weight percent. The halogen may be bromine, chlorine, and mixtures thereof. Preferably, the halogen is bromine. The major portion of the halogen is chemically bound to the para-alkyl group, that is, the halogen-containing copolymer comprises para-

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range of compositions thereof. At least about 95 weight percent of the copolymer product has a para-alkylstyrene content within about 10 wt. percent, and preferably within about 7 wt. percent, of the average para-alkylstyrene content for the overall composition, and preferably at least about 97 wt. percent of the copolymer product has a para-alkylstyrene content within about 10 wt. percent and preferably within about 7 wt. percent, of the average para-alkylstyrene content for the overall composition. This substantially homogeneous compositional uniformity thus particularly relates to the intercompositional distribution. That is, with the specified copolymers, as between any selected molecular weight fraction the percentage of para-alkylstyrene therein, or the ratio of para-alkylstyrene to isoolefin, will be substantially the same, in the manner set forth above.

In addition, since the relative reactivity of para-alkylstyrene with isoolefin such as isobutylene is close to one, the intercompositional distribution of these copolymers will also be substantially homogeneous. That is, these copolymers are essentially random copolymers, and in any particular polymer chain the para-alkylstyrene and isoolefin units will be essentially randomly distributed throughout that chain.

The halogen-containing copolymers useful in the practice of the present invention have a substantially homogeneous compositional distribution and include the para-alkylstyrene moiety represented by the formula:

styrene copolymers suitable for use in the process of the present invention. The polymerization temperature may range from about minus 35°C to about minus 100°C, preferably from about minus 40 to about minus 80°C.

The processes for producing the copolymers can be carried out in the form of a slurry of polymer formed in the diluents employed, or as a homogeneous solution process. The use of a slurry process is, however, preferred, since in that case, lower viscosity mixtures are produced in the reactor and slurry concentration of up to 40 wt. percent of polymer are possible.

The copolymers of isomonoolefins and para-alkylstyrene may be produced by admixing the isomonoolefin and the para-alkylstyrene in a copolymerization reactor under copolymerization conditions in the presence of a diluent and a Lewis acid catalyst.

Typical examples of the diluents which may be used alone or in a mixture include propane, butane, pentane, cyclopentane, hexane, toluene, heptane, iso-octane, etc., and various halohydrocarbon solvents which are particularly advantageous herein, including methylene, chloride, chloroform, carbon tetrachloride, methyl chloride, with methyl chloride being particularly preferred.

An important element in producing the copolymer is the exclusion of impurities from the polymerization reactor, namely, impurities which, if present, will result in complexing with the catalyst or copolymerization with the isomonoolefins or the para-alkylstyrene, which in turn will prevent one from producing the para-alkylstyrene copolymer product useful in the practice of the present invention. Most particularly, these impurities include the catalyst poisoning material, moisture and other copolymerizable

halogenation conditions be chosen to avoid diluent halogenation, and that residual para-methylstyrene has been reduced to an acceptable level.

With halogenation of para-methylstyrene/ isobutylene copolymers; it is possible to halogenate the ring carbons, but the products are rather inert and of little interest. However, it is possible to introduce halogen desired functionality into the para-methylstyrene/ isobutylene copolymers hereof in high yields and under practical conditions without obtaining excessive polymer breakdown, cross-linking or other undesirable side reactions.

It should be noted that radical bromination of the enchainied para-methyl styryl moiety in the useful copolymers for the practice of this invention can be made highly specific with almost exclusive substitution occurring on the para-methyl group, to yield the desired benzylic bromine functionality. The high specificity of the bromination reaction can thus be maintained over a broad range of reaction conditions, provided, however, that factors which would promote the ionic reaction route are avoided (i.e., polar diluents, Friedel-Crafts catalysts, etc.).

Thus, solutions of the suitable para-methylstyrene/isobutylene copolymers in hydrocarbon solvents such as pentane, hexane or heptane can be selectively brominated using light, heat, or selected radical initiators (according to conditions, i.e., a particular radical initiator must be selected which has an appropriate half-life for the particular temperature conditions being utilized, with generally longer half-lives preferred at warmer hydrogenation temperatures) as promoters of radical halogenation, to yield almost exclusively the desired benzylic bromine functionality, via substitution on the para-methyl group, and without appreciable chain scission and/or crosslinking.

bromine functionality in the monobromo form can be introduced into the above stated copolymers, up to about 60 mole percent of the para-methylstyrene content.

It is desirable that the termination reactions be minimized during bromination, so that long, rapid radical chain reactions occur, and so that many benzylic bromines are introduced for each initiation, with a minimum of the side reactions resulting from termination. Hence, system purity is important, and steady-state radical concentrations must be kept low enough to avoid extensive recombination and possibly cross-linking. The reaction must also be quenched once the bromine is consumed, so that continued radical production with resultant secondary reactions (in the absence of bromine) do not then occur. Quenching may be accomplished by cooling, turning off the light source, adding dilute caustic, the addition of a radical trap, or combinations thereof.

Since one mole of HBr is produced for each mole of bromine reacted with or substituted on the enchainued para-methylstyryl moiety, it is also desirable to neutralize or otherwise remove this HBr during the reaction, or at least during polymer recovery in order to prevent it from becoming involved in or catalyzing undesirable side reactions. Such neutralization and removal can be accomplished with a post-reaction caustic wash, generally using a molar excess of caustic on the HBr. Alternatively, neutralization can be accomplished by having a particulate base (which is relatively non-reactive with bromine) such as calcium carbonate powder present in dispersed form during the bromination reaction to absorb the HBr as it is produced. Removal of the HBr can also be accomplished by stripping with an inert gas (e.g., N<sub>2</sub>) preferably at elevated temperatures.

two types are particularly preferred. Alternatively, non-black fillers and pigments may be used for white tire sidewalls. The blends are cured with conventional curatives for highly unsaturated or chlorobutyl rubbers, including sulphur, alkylphenol disulphide, zinc oxide, sulphenamide derivatives, guanidines, benzothiazyldisulphide (MBTS) and mercaptobenzothiazole (MBT).

The tire sidewall composition of the present invention may be vulcanized by subjecting it to heat and/or light or radiation according to any vulcanization process. Typically, the vulcanization is conducted at a temperature ranging from about 100°C to about 250°C, preferably from about 140°C to about 200°C, for a time period ranging from one minute to several hours.

The tire sidewall composition of the present invention may be used in producing sidewall for tires, for example, motor vehicle tires such as truck tires, bus tires, passenger automobile, motorcycle tires, and the like.

Suitable tire sidewall compositions may be prepared by using conventional mixing techniques including, e.g., kneading, roller milling, extruder mixing, internal mixing (such as with a Banbury® mixer), etc. The sequence of mixing and temperatures employed are well known to the skilled rubber compounder, the objective being the dispersion of fillers, activators and curatives in the polymer matrix without excessive heat buildup. A useful mixing procedure utilizes a Banbury mixe in which the rubber components, fillers, and plasticizer are added and the composition mixed for the desired time or to a particular temperature to achieve adequate dispersion of the ingredients. Alternatively, the rubbers and a portion of the fillers (e.g., one-third to two-thirds) is mixed for a short time (e.g., about 1 to 3 minutes) followed by the remainder of the fillers and oil. Mixing is continued for about 5 to 10 minutes at high rotor speed during which time

Example 1

A tire sidewall composition was prepared by compounding the components as set forth in Table I (Banbury size B) using a mix cycle as shown below. Composition 1-1 is a "control" or reference composition, not a composition of the present invention.

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Table II

	<u>1-1</u>	<u>1-2</u>	<u>1-3</u>	<u>1-4</u>
<b>Static Ozone</b>				
<u>100 pphm, 30°C, 660kPa Stress</u>				
Time to Failure, h	<24	160	>300	>300
<b>Dynamic Ozone*</b>				
<u>100 pphm, 0-20% ext, 30°C</u>				
Time to Failure, h	48	>288	>288	>288
<b>Fatigue Crack Propagation*</b>				
<u>DC/DN at 15% Strain, 60°C</u>				
In air, Nm/cyc	30.9	26.2	20.4	16.2
In Ozone, Nm/cyc	48.5	40.8	22.9	18.0

\*Dynamic ozone and fatigue crack propagation tests are described in an article by D.G. Young in Rubber Chemistry and Technology - Vol. 58, No. 4.

Blends 1-3 and 1-4 exhibited better ozone resistance and low fatigue crack propagation.

#### Example 2

Sidewall blend compositions were prepared according to the procedure of Example 1 as shown in Table III.

Example 3

Tire sidewall blend compositions were prepared, generally according to the procedure of Example 1, using the formulations shown in Table V. The compositions used brominated copolymers of isobutylene-paramethylstyrene, variations in the type and concentration of the highly unsaturated rubbers as well as variations in carbon black type and curative concentration. The variations are within the scope of the invention and represent preferred compositions useful as tire sidewall components. Properties of the compositions are shown in Table VI.

Table V

Composition No.	3-1	3-2	3-3	3-4
Natural Rubber (SMR 5)	30	30	25	25
BR 1207	30	30	35	40
BrIB-PMS B <sup>1</sup>	40	--	40	35
BrIB-PMS C <sup>2</sup>	--	40	--	--
N660 Black	50	50	50	--
N351 Black	--	--	--	40
Flexon 641 Oil	12	12	12	12
Escorez 1102 Resin	5	5	--	--
SP 1077 Resin	--	--	5	5
Stearic Acid	2	2	1	1
Zinc Oxide	3	3	1	1
Sulfur	0.4	0.4	1.0	1.0
Vultac 5	1.5	1.5	0.8	0.8
MBTS	1.7	1.7	0.75	0.75

1. Brominated isobutylene-paramethylstyrene copolymer: 5 wt.% paramethylstyrene, 1.95 wt.% bromine and a Mooney viscosity at 125°C of 29.

2. Brominated isobutylene-paramethylstyrene copolymer: 10 wt.% paramethylstyrene, 1.95 wt.% bromine and a Mooney viscosity at 125°C of 29.

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Copolymer A was a halogenated copolymer of isobutylene and para-methylstyrene containing 10 wt.% para-methylstyrene moieties, 2.5 wt.% bromine, a Mooney viscosity at 125°C of 46, and 1.5 mole % brominated para-methylstyrene moieties. Copolymer B was a copolymer of isobutylene and a para-methylstyrene containing 15 wt.% para-methylstyrene moieties; 2.0 wt.% bromine, a Mooney viscosity at 125°C of 50, and 1.1 mole % brominated para-methylstyrene moieties.

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TABLE VIII

<u>Properties</u>	<u>Compositions</u>					
	4-1	4-2	4-3	4-4	4-5	4-6
Mooney Scorch, 135°C						
Min. to 5pt. Rise	24.3	20.3	15.0	15.2	15.8	18.8
Mooney Viscosity						
ML - 1+4' @ 100°C	45	46	46	46	46	44
Rheometer - 160°C						
MH, in. - lb.	43.0	43.1	45.5	42.0	43.3	39.8
ML, in. - lb.	7.5	6.8	4.5	4.8	5.0	7.0
ts2, min.	5.8	5.9	4.7	4.7	4.6	4.7
tc90, min.	23.2	21.8	20.8	15.2	14.8	20.8
Tensile, MPa	13.1	13.4	13.2	14.2	14.1	9.3
300% Modulus, MPa	4.5	6.4	6.5	5.4	5.5	4.3
% Elongation	700	620	530	640	627	603
Shore A Hardness	55	55	57	56	57	52
Dynamic Ozone						
100 pphm, 20% Ext.	500+	500+	500+	500+	500+	500+
Hrs. to Crack						
Static Ozone						
100 pphm, Bent Loop	500+	500+	500+	500+	500+	500+
Hrs. to Crack						
Strip Adhesion - Kn/m. (Tc90 + 5' @ 160°C)						
To black sidewall:						
@ RT	4.5	3.9	4.0	3.9	5.9	3.6
@ 100°C	2.0	2.0	1.7	2.1	3.1	1.5
	T	T	T	T	T	T
Outdoor Flex (Pierced Only)	500+	500+	500+	500+	500+	500+
Weatherometer						
Hrs. to Crack	700+	700+	700+	700+	700+	700+

Example 5

White sidewall compositions were prepared by compounding the components shown in Table X using the mix cycle shown in Example 4. Copolymer C was a brominated copolymer of isobutylene and para-methylstyrene containing 15 wt.% para-methylstyrene moieties and 2 wt.% bromine. Copolymer D was a brominated copolymer of isobutylene and para-methylstyrene containing 10 wt.% para-methylstyrene moieties and 2 wt.% bromine. Copolymer E was a brominated copolymer of isobutylene and para-methylstyrene containing 7.5 wt.% para-methylstyrene moieties and 2 wt.% bromine. Copolymer F was a copolymer of isobutylene and para-methylstyrene containing 5 wt.% para-methylstyrene moieties and 1 wt.% bromine.

Table X

<u>Composition No.</u>	<u>5-1</u>	<u>5-2</u>	<u>5-3</u>	<u>5-4</u>	<u>5-5</u>	<u>5-6</u>	<u>5-7</u>	<u>5-8</u>
Copolymer C	50	--	--	--	--	--	--	35
Copolymer D	--	60	--	50	--	--	--	--
Copolymer E	--	--	--	--	60	50	35	--
Copolymer F	--	--	70	--	--	--	--	--
Natural Rubber	50	40	30	50	40	50	65	65
TiO <sub>2</sub>	25	25	25	25	25	25	25	25
Nucap 290	32	32	32	32	32	32	32	32
Mistron Vapor Talc	34	34	34	34	34	34	34	34
Sunolite 240 Wax	3	3	3	3	3	3	3	3
Stearic Acid	1	1	1	1	1	1	1	1
Ultramarine Blue	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Escorez 1102	4	4	4	4	4	4	4	4
Zinc Oxide	3	3	3	3	3	3	3	3
Sulfur	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Vultac #5	1.0	1.3	1.3	1.3	1.3	1.3	1.3	1.3
MBTS	1.3	1.0	1.0	1.0	1.0	1.0	1.0	1.0

The tire sidewall compositions of Table X were tested for various properties. The results of the tests are shown in Table XI.

As can be seen from Table XI, Compositions 5-1 through 5-8, which were compositions in accordance with the present invention comprising the preferred ratios of components, had particularly improved properties, such as ozone resistance, resistance to cracking, and good adhesion to tire carcass.

A description of ingredients used in the above examples that are not otherwise described is shown in Table XII.

Table XII

<u>Ingredient</u>	<u>Description</u>	<u>Supplier</u>
Escorez 1102	Petroleum hydrocarbon tackifier resin	Exxon Chemical Americas
Flectol H	Polymerized 1,2 dihydro- 2,2,4-trimethylquinoline	Harwick Chemical Corp.
Flexon 641 Oil	Naphthenic petroleum oil (ASTM Type 103)	Exxon Co., USA
Santocure MOR	2-(morpholinothio)benzo-thiazole	Monsanto Chemical Co.
Santoflex 13	N,N'-phenyl-p-phenylene diamine	Monsanto Chemical Co.
SP 1077 Resin	Alkyl phenolformaldehyde resin	Schenectady Chemicals
Sunolite 240 Wax	Blend of petroleum waxes	Witco Chemical
Vultac 5	Alkyl phenol disulfide on inert carrier	Pennwalt Chemical
Wood Rosin FF	Thermoplastic naval stores tackifying resin	Harwick Chemical Corp
Nucap 290	Mercaptosilane functionalized hydrated aluminum silicate	J. M. Huber
Mistrion Vapor	Magnesium silicate organo-functional surface modified	Cyprus Industrial Minerals
CIIR 1066	Chloro-isobutene-isoprene	Exxon Chemical, USA
Ultramarine Blue	Powdered pigment	AKROCHEM

8. The tire sidewall of claim 1, wherein said tire sidewall composition is a white composition, and wherein said composition comprises non-black additives selected from the group consisting of fillers, pigments, and mixtures thereof.

9. The tire sidewall composition of claim 1, wherein said halogen-containing copolymer comprises from about 0.5 to bout 20 weight percent of said para-alkylstyrene.

10. The tire sidewall composition of claim 1, wherein said halogen-containing copolymer comprises from above zero to about 7.5 weight percent of said halogen.

11. The tire sidewall composition of claim 1 wherein said halogen-containing copolymer comprises from about 1 to about 7.5 weight percent of said halogen.

12. The tire sidewall composition of claim 1, wherein said halogen is selected from the group consisting of chlorine, bromine, and mixtures thereof.

13. The tire sidewall composition of claim 1, wherein said halogen comprises bromine and wherein said bromine is chemically bound to said para-alkylstyrene.

14. The tire sidewall composition of claim 1 wherein said halogen-containing copolymer is a bromine-containing copolymer of isobutylene and para-methylstyrene.

15. A vulcanized tire comprising a sidewall made of a composition comprising from about 10 to about 90 weight parts per hundred parts of total rubber of at least one unsaturated rubber selected from the group consisting of natural rubber, polyisoprene, styrene butadiene rubber, polybutadiene rubber, and mixtures thereof, and from about 10 to about 90 weight parts per hundred parts of total rubber of a halogen-containing copolymer of a C<sub>4</sub> to C<sub>7</sub> isomonoolefin and a para-alkylstyrene.

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25. The vulcanized tire of claim 15, where said halogen is selected from the group consisting of chlorine, bromine, and mixtures thereof.

26. The vulcanized tire of claim 15, where said halogen comprises bromine and wherein said bromine is chemically bound to said para-alkylstyrene.

27. The vulcanized tire of claim 15, where said halogen-containing copolymer is a bromine-containing copolymer of isobutylene and para-methylstyrene.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9105666  
SA 51606**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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